Current approaches to *pn* junctions in wider band gap II–VI semiconductors

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Long-standing problems to make junctions in wider band gap semiconductors, especially II–VIs, are being restudied today by new low-temperature epitaxial growth methods, which may lead to current-injecting devices suited to light emission. This paper reviews various approaches briefly, with particular emphasis on heterojunctions and methods to control dopants. A few of the many possible heterojunctions are favored by small offset barriers, but are not without other problems. New dopants, besides the much-studied Li, are being introduced in new ways, in the effort to attain reproducibility and stability.

I. INTRODUCTION

Devices made from narrow band gap II-VI materials have been one of the great success stories of recent years. Unfortunately, however, this success has not extended to the wider band gap II–VIs. A reason often given for this is our inability to produce *pn* junctions in these wider band gap materials. The situation can be viewed as in Fig. 1, which compares the number of papers on zinc chalcogenides with those on silicon. In the early 1920's, when Si was largely an additive in steelmaking, the Zn chalcogenides already had substantial uses as light emitters, often in cathodoluminescence. With the revolution begun by *pn* junctions about 1950, however, the Zn-based materials began a long relative decline. Today, however, there are good prospects that low-temperature epitaxial growth technologies can ease such difficulties in the chalcogenides and facilitate their capabilities for light emission throughout the visible.

The difficulty to produce *pn* junctions in semiconducting materials is not an exclusive problem of the II–VIs, as is indicated in Fig. 2. Common elemental and binary semiconductors which permit *pn* junctions by conventional processing are formed from elements in the highlighted portion of the periodic chart shown. Those which do not permit junctions have at least one component from outside the highlighted region. It should be noted, however, that the boundary drawn between these two regions is not beyond argument today, nor change tomorrow. Indeed it could be argued already that ZnSe should fall within the highlighted region.

In Fig. 2 the column IV semiconductors appear to be most amenable to *pn* junctions. Indeed SiC has been much studied as a blue light emitter, with commercial production at times. It does have the practical drawback, however, that processing temperatures above 2000 °C are usually required. The III–Vs, of course, have been a great success as light emitters, indeed to the point of lasing, and are presently being intensively pursued into the visible range. Last, the II–VIs, in spite of their early uses as light emitters, are still awaiting a solution to the *pn* junction problem.

Reasons that many II–VIs cannot be made both *p* and *n* type have long been sought. Thermodynamic analyses comparing band gap energy to formation energy were an early theme and led to a thermochemistry of defects in these materials.[1] Later careful photoluminescence studies by Dean,[2] however, found not the expected defect species, but instead trace impurities in otherwise high purity material. This latter discovery led to serious attempts to produce II–VI materials of very high purity, as a partial solution to the doping problem. More recently, structural problems have been proposed to play a major role, particularly in lattice relaxation around dopants[3] and in the special properties of twin planes.[4,5] While each of these views suggests certain remedies, most experimental efforts have focused on the use of heterojunctions and the control of doping to overcome the junction difficulty. This paper will be mainly devoted to these two approaches.

II. HETEROJUNCTION APPROACH

One way to overcome the difficulty of making *pn* junctions is to join a *p*-type II–VI to an *n*-type II–VI to form a heterojunction (HJ). Such a structure contains a *pn* junction, by definition. Whether such a HJ will be able to inject current under moderate forward bias, as desired in light-

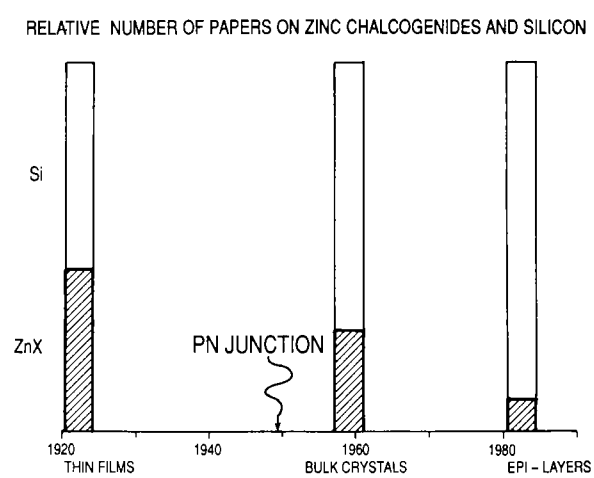

FIG. 1. Papers on ZnS, ZnSe, and ZnTe vs papers on Si at various times in this century. First two bar graphs from Chemical Abstracts and last from Dialog.

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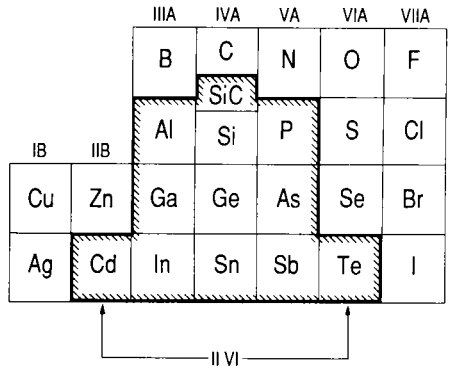

FIG. 2. The common II–VI, III–V, and IV semiconductors which allow *pn* junctions by conventional processing are formed from elements enclosed by the heavy line. Thus CdTe and GaP conventionally afford *pn* junctions, whereas ZnTe and GaN do not.

emitting structures, however, depends very much on the magnitude of the band offsets for that particular HJ.

The particular HJ most intensively investigated has been *n*-ZnSe/*p*-ZnTe. The studies of Aven and co-workers[6] in the 1960s included the ternary $ZnSe_xTe_{1-x}$ which easily forms by interdiffusion in the HJ, especially during growth by the liquid phase epitaxy method then widely used. As discussed in detail by Fujita *et al.*[7] this layer then could easily dominate electrical properties, especially through "interface states." Incidentally, this situation, while not optimum for carrier injection across a HJ, can still be quite useful for back contacts.

With the advent of molecular-beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD) offering growth temperatures as low as 200 °C in the last few years, the thickness of interdiffusion layers can now be greatly reduced. Thus, for example, the ZnSe/ZnTe HJ of Konagai and co-workers[8] grown by MBE recently can be considered abrupt, as is the case for several other II–VI/II–VI HJ. At the same time, both theory and experiment are offering values for the band offsets to be expected for the abrupt HJ. This rather attractive situation is counterbalanced, however, by fairly large variations[9] in the predicted offset values from among the dozen or so sets of predictions available today.

We begin with the theoretically predicted values of Harrison and Tersoff,[10] shown in Fig. 3. The plotting scheme used in this figure shows for any HJ the band offsets, degree of lattice mismatch and dopability of each material. For example, Fig. 3 predicts the much-studied ZnSe/ZnTe HJ to be type I with moderate sized offsets, with one member *p* dopable and one *n* dopable, and with about 7% lattice mismatch. As will be discussed later, this prediction is moderately optimistic; it says that current injection into the smaller band gap ZnTe should occur easily.

Another prediction from Fig. 3 is that the *p*-ZnTe/*n*-AlSb HJ is type II with the desirable, but unusual property that both offsets are "negative," i.e., injected carriers lose energy on crossing the interface. This puts this HJ on a par with homojunctions for injecting carriers.[11] As is discussed in detail elsewhere,[9] the relative magnitude of the two injected currents in such cases depends primarily on doping of the *p* and *n* regions, and thus, in principle the HJ can be designed for the usually preferred injection into the wider band gap material. Substantial practical problems are present in this HJ, however. If the HJ is not perfectly abrupt, severe cross-doping effects can occur from the combining of II–VI and

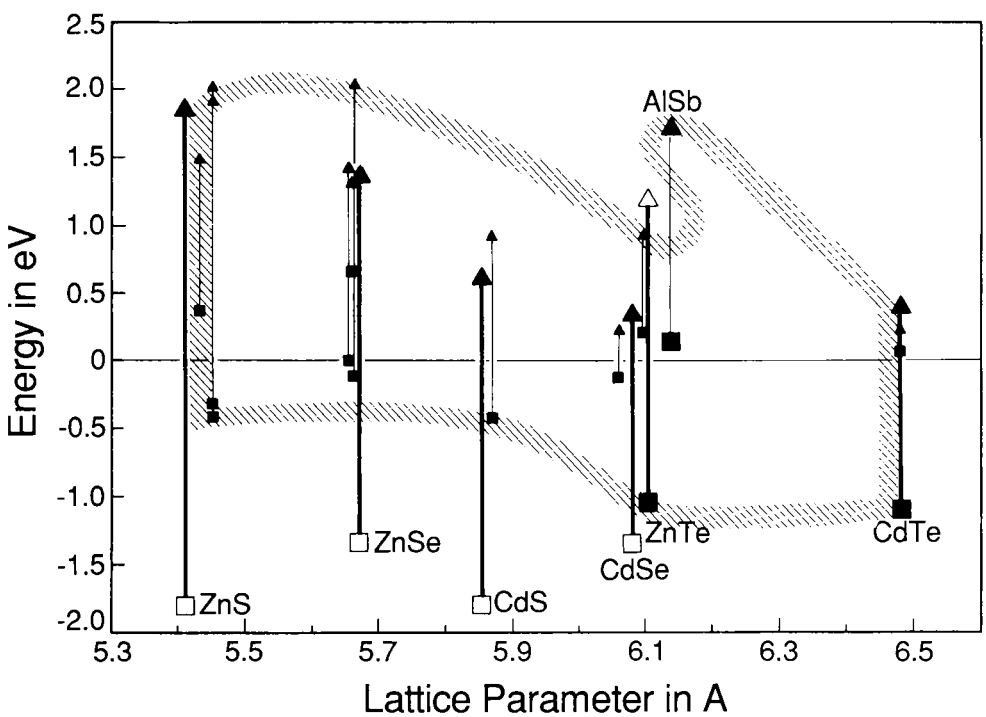

FIG. 3. Energy relationships, according to Harrison and Tersoff, for the band edges of common semiconductors. Only II–VI compounds and AlSb are labeled. Abscissa is the lattice parameter of cubic structures, or, for Wurtzite structures, equivalent parameter on basal plane. Squares denote valence band edges and triangles conduction band edges. Vertical lines represent band gap. Material that conventionally cannot be made usefully *p* type or *n* type is denoted by the appropriate open symbol; otherwise, filled symbols are used. Hatching is drawn to highlight regions free of open symbols. Zero of energy is arbitrarily set at E_v(GaAs).

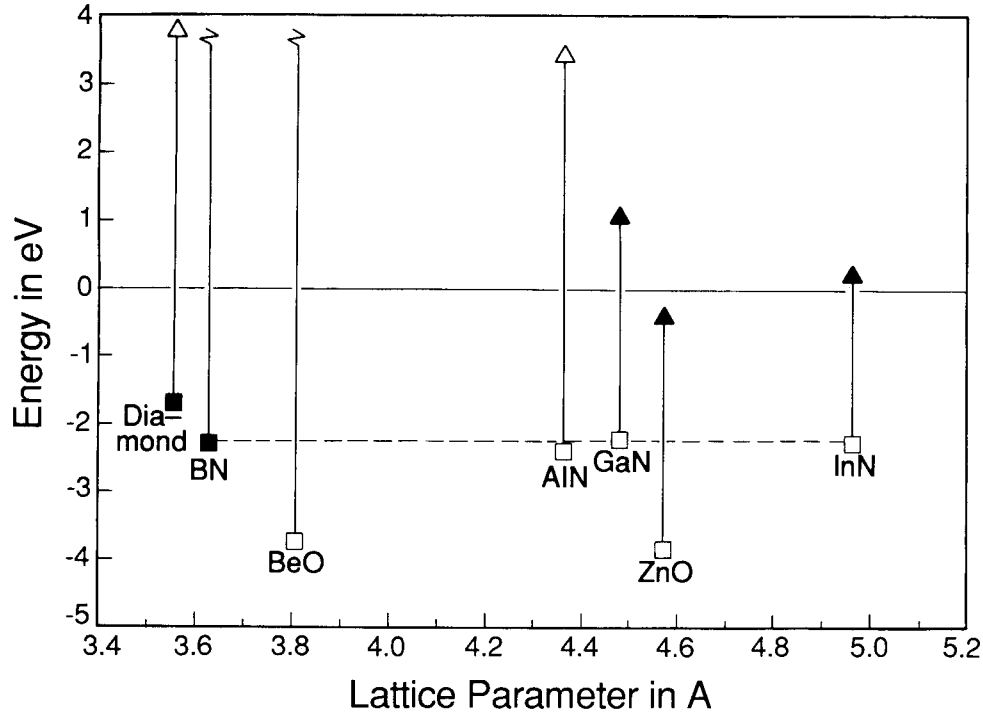

FIG. 4. Plot similar to Fig. 3 except at smaller lattice parameters. The BN shown is the dense, cubic form. Dashed line indicates an interesting relationship among the nitrides (see text).

III–V materials at a HJ. Earlier studies on this point give a mixed prognosis, with the work of Kowalczyk *et al.*[12] on ZnSe/GaAs in good agreement with theoretical expectations, though some variability due to processing details was noted. In the case of the CdS/InP HJ, however, a larger variation, ~0.5 eV, on processing has been reported.[13,14] Also a recent study of the ZnTe/GaSb HJ in which a small diffusion of Ga into the ZnTe was detected showed offsets at large variance with all the predictions that have been made for this HJ[15]. Growth studies by Yao *et* al[16], however, open the possibility that the variance may result from the substrate orientation and reconstruction used.

The Harrison Tersoff predictions suggest a third interesting HJ possibility. At smaller lattice parameters the predictions are as pictured in Fig. 4, and suggest that both diamond, which has recently been rendered 0.01 Ω cm *p* type,[17] and cubic BN should be good thermionic hole injectors. The only other prediction for these materials, due to Harrison,[18]

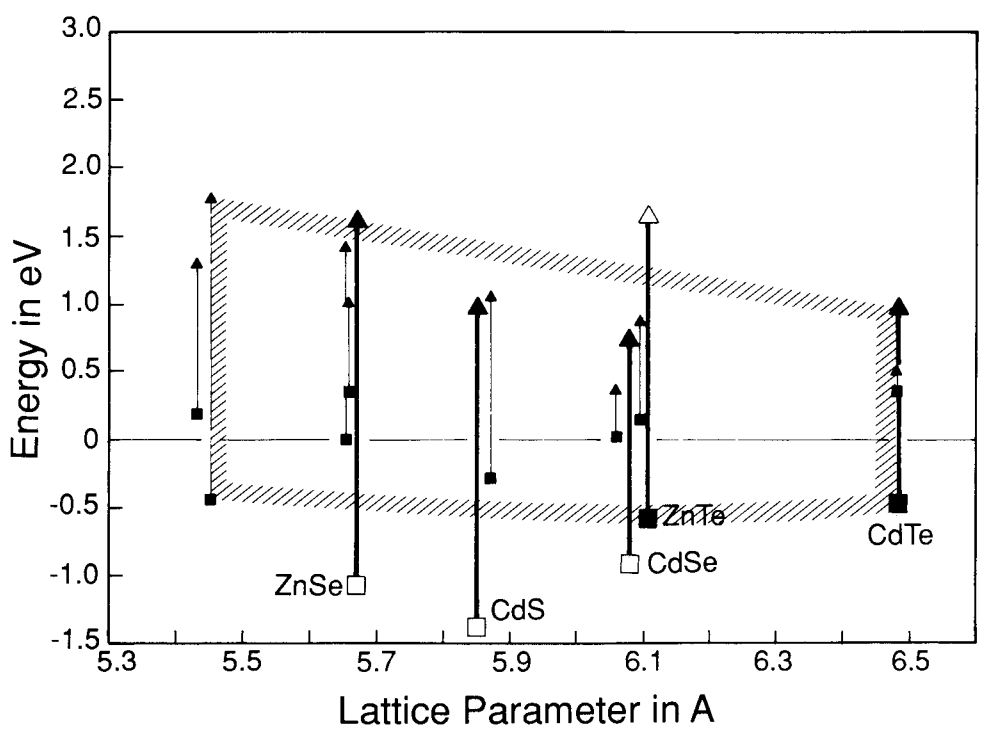

FIG. 5. Plot similar to Fig. 3, except that the energy relationships of Katnani and Margaritondo are shown.

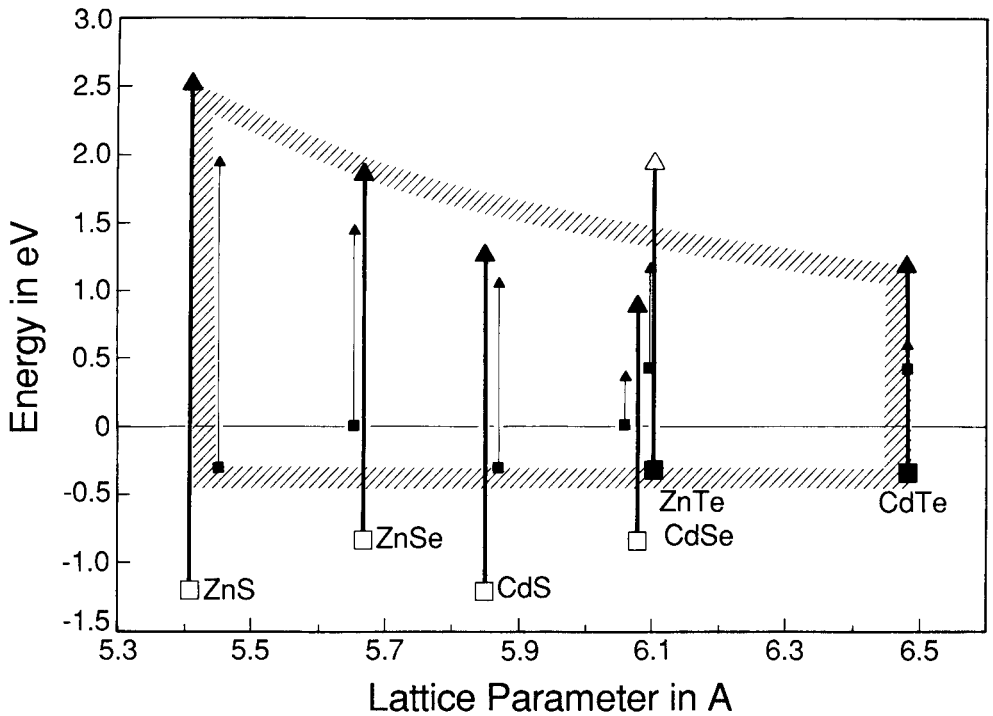

FIG. 6. Plot similar to Fig. 3, except that the energy relationships of McCaldin, McGill, and Mead are shown.

is in agreement on this point. From such predictions, one concludes, for instance, that BN would have approximately zero valence band offsets against other nitrides in the figure, including GaN which has been seriously considered for a blue light emitter. Also, more relevant to the present discussion, BN would see a negative valence band offset against the sulfides and selenides in Fig. 3. The huge lattice mismatches involved in such HJs, however, would likely preclude pseudomorphic growth.

Experimentally determined values for band offsets have also been presented. Probably the most widely quoted are the photoemission-based values of Katnani and Margaritondo[19] shown in Fig. 5. An alternative experimental approach is to use the Schottky barrier height ϕ_p between the noble metal gold and the p-type semiconductors to locate valence band positions E_v. This approach, which has been in and out of favor over the years, began with a graph of ϕ_p values by McCaldin, McGill and Mead[20] in 1976, plotted in the present format in Fig. 6. Recently, arguments for the correlation between ϕ_p and E_v have been advanced by Tersoff.[21] The experimental values shown in Figs. 5 and 6 share predictions for 11 semiconductors. The root-mean-square (rms) deviation between the two sets of predictions is 0.11 eV, which is about the experimental uncertainty usually encountered in such measurements. Yet other experimental values, including the electron affinity values of Freeouf and Woodall[22] and Kroemer's selected values,[23] are in somewhat larger disagreement[9] with Katnani and Margaritondo.[19]

The experimental and theoretical predictions just discussed are pictured for the ZnSe/ZnTe HJ in the flat band diagram of Fig. 7. All three predictions are favorable for electron injection into the p-ZnTe, though in one case a small barrier of 0.06 eV is present. Also all three predictions agree that there is a significant barrier against hole injection into the n-ZnSe. Even the most favorable prediction for hole injection indicates a barrier of 0.29 eV, which would be quite difficult to counterbalance by very heavy doping of the ZnTe and light doping the ZnSe. The more extensive predictions for this HJ considered in Ref. 9 tend to come mostly to the same or somewhat less optimistic conclusions.

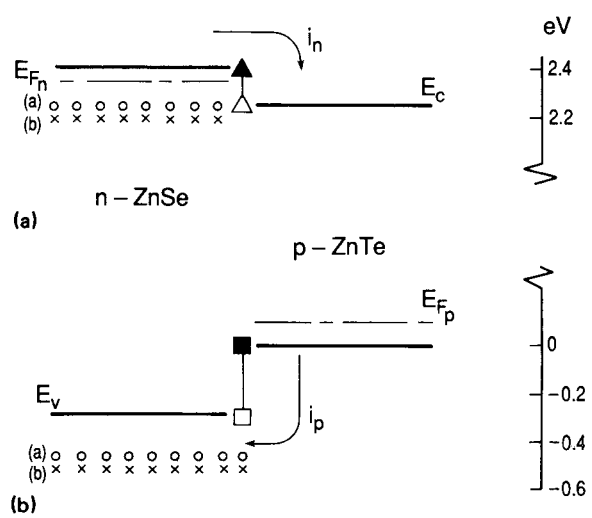

FIG. 7. Energy relationships for the n-ZnSe/p-ZnTe heterojunction. Symbols and heavy lines are positioned according to Harrison and Tersoff's values shown in Fig. 3. E_c and E_v are conduction and valence band edges, respectively. The quasi-Fermi levels, E_{Fn} and E_{Fp}, are shown schematically. Injection currents are denoted by i_n and i_p. (a) positions band edges according to Katnani and Margaritondo (Fig. 5), whereas (b) positions them according to McCaldin, McGill, and Mead (Fig. 6).

III. DOPING CONTROL APPROACH

While there is much controversy on the causes for the limited dopability shown in several earlier figures, it is now quite clear that this limitation does *not* arise from lack of shallow dopants. Indeed tabulations[24,25] of dopant energy levels show a *choice* of several shallow levels where needed. But the shallow levels are almost always compensated by opposing charges, arising from defects, impurities or more complex entities envisaged in the various models mentioned earlier. Due to compensation, then, the Fermi level is not brought near the desired shallow levels, i.e. does not move beyond the "hatched" regions of earlier figures.

To overcome the compensation phenomenon several physical approaches continue to be tried. These are mentioned here with brief comments on present status:

(i) Grow defect free. In the spirit of Kroger's model[1] certain defects can be diminished, for example by stoichiometry control. This approach undoubtedly helps, but compensation still persists.

(ii) Grow pure. As suggested by Dean's work,[2] removal of impurities participating in compensation can help. With the heavier doping usually needed in devices, however, purification appears not to overcome compensation.

(iii) Quench. In ZnTe, for example, both *p*- and *n*-type material exist at elevated temperatures.[26] Fast quenching may be able to freeze in the desired *n*-type material. A quenching experiment[27] made with ZnTe produced *n*-type material but of very high resistivity.

(iv) Photoassisted doping. This technique applied during MBE[28] has increased carrier concentrations substantially in CdTe and may be extendable to larger bandgap material.

(v) Drift. Electric fields readily move mobile species like interstitial Li. Experiments[29,30] to drift interstitial Li, however, apparently move more than the intended interstitials[30] and compensation is still present.

Much attention today is given to the choice of shallow level dopant. Extensive studies in Grenoble[31] on the behavior of the mobile dopant Li in ZnTe revealed many interactions between the mobile dopant, on the one hand, and Te precipitates, lineal boundaries and perhaps other structures, on the other. Also the interactions exhibited temperature dependencies, so that a complex that served as a sink at one temperature could become a source at another temperature.[31] Thus very mobile dopants, unless processed under very limited constraints, tend to produce complex structures.

A broad view of diffusivities is presented in Fig. 8, which spans temperatures from room temperature to the melting point of Si. On the scale of this figure, the range characterizing the standard substitutional dopants in Si appears narrow, in enormous contrast to that of interstitial Li in Si. For comparison with II–VIs, a CdTe host is selected, because of the availability of data in the recent review of Shaw.[32] More complication is immediately evident in the II–VI case. For In dopant, two lines are shown for different stoichiometric conditions. A further complication, not shown, is an apparently temperature-independent diffusivity of In the 200 °C to 400 °C range. To obtain diffusivities for interstitial Li in a CdTe host, a model had to be invoked to distinguish between interstitial and substitutional Li. Perhaps more important, however, is to note that the distinction between substitutional and interstitial, so dramatic in the case of a Si host, is less obvious for CdTe. This suggests that changing dopant may not make as drastic an improvement in diffusive behavior in II–VIs as would be the case in Si or Ge. Ultimately one would like to use dopants with diffusivities of 10^{-16} cm^2 sec^{-1} or less at processing temperature, as is done with Si where the "rule of thumb" for much conventional processing is that after cooling Si below 850 °C dopants become frozen in.

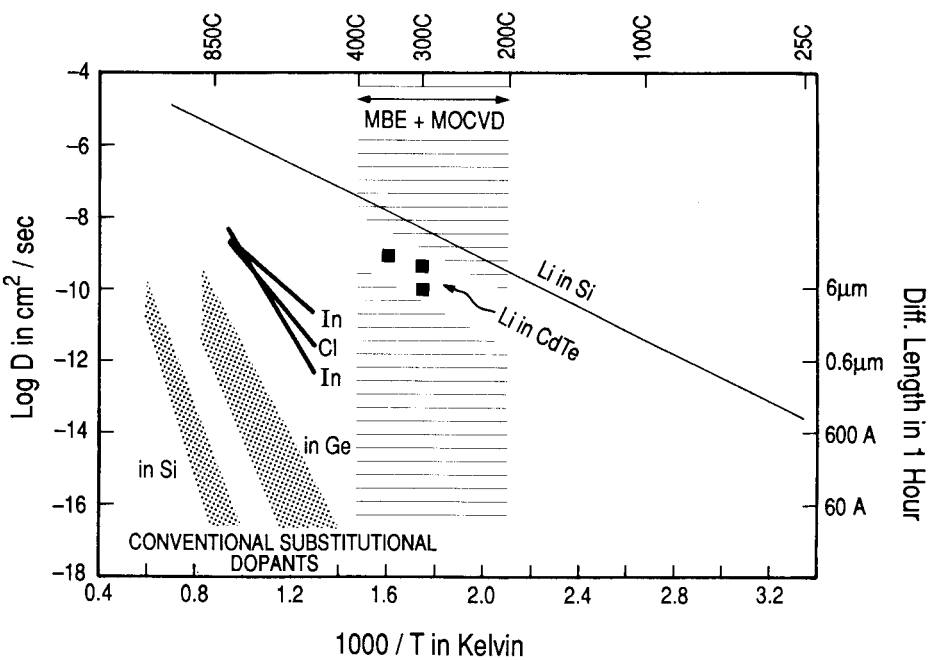

FIG. 8. Diffusivities over a wide temperature range. Stipling shows the range of diffusivities for the widely used substitutional donors and acceptors in Si and Ge. Heavy lines and squares are diffusivities in CdTe host, according to Shaw's review. Of the two lines for In diffusant, the steeper one is for Cd-saturated conditions and the shallower for Te saturation. Squares represent diffusivity of *interstitial* Li. For reference, the well established diffusivity of Li in Si is shown, as well as the temperature range currently emphasized in epitaxial growth.

TABLE I. Recent reports of *p*-type ZnSe.

Reference	Acceptor Li	Na	N	O	Remarks
35	X		X		MOCVD + Li_3N
36			X		low energy ion doping
37	X				MBE
38	X				MOCVD
39			X		MOCVD + NH_3
40			X		MOCVD + NH_3
41			X		MOCVD + NH_3
42	X				Implant
43					Iodine dopant?
44				X	MBE + ZnO
45			X		Implant
46		X			Implant

The most extensive efforts in the control of dopants today are occurring in the case of *p*-ZnSe. This material, as mentioned earlier, appears to be on the verge of becoming a "conventional" material, if reproducibility and stability problems can be solved. It has been studied for many years and compilations by Ruda[33] and Bhargava[34] indicate the dopant of choice in earlier time periods to be Li.

Recent reports[35–46] of *p*-ZnSe, roughly since the compilation of Bhargava,[34] are presented in Table I. Today efforts are being made to use acceptors less mobile than Li. Sodium, for example, should be both less mobile and less soluble,[29] the latter aspect requiring special introduction methods like implantation. Nitrogen is expected to be not only less mobile than Li, but also a good choice from among column V acceptors in minimizing deep levels.[3,40,45] Also of interest is the new use of implantation at moderate or low energies. Possibly implantation during MBE growth, as in the work of Ohkawa *et al.*[36] may also help. Overall, the use of new dopants and methods of introducing them is perhaps the biggest change now occurring in the wide gap II–VIs.

IV. SUMMARY

The limitation that many wide bandgap semiconductors do not afford both *p*- and *n*-type doping, so that *pn* junctions cannot be obtained, is especially restrictive for the II–VIs. Today, however, epitaxial growth at temperatures as low as 200 °C may relax this restriction, enabling *pn* heterojunctions to inject carriers, as well as enabling new control of dopants so that *pn* homojunctions become feasible.

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